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This article was submitted to
Plutonium Futures-The Science Conference, Albuquerque, NM, July
6-10, 2003

February 19, 2003

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This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Plutonium Colloid-Facilitated Transport in the Environment – Experimental and Transport Modeling Evidence for Plutonium Migration Mechanisms

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Introduction

Natural inorganic colloids (< 1 micron particles) found in groundwater can sorb low-solubility actinides and may provide a pathway for transport in the subsurface. For example, Kersting et al.¹ found that Pu, associated with colloids fraction of the groundwater, was detected over 1 km away from the underground nuclear test at the Nevada Test Site (NTS) where it was originally deposited 28 years earlier. However, laboratory experiments have not identified the mechanisms by which Pu may sorb to colloids or exist as its own colloid and travel relatively unimpeded in the subsurface. Some data suggest that Pu sorption to colloids is a very fast process while desorption is very slow or simply does not occur.² Slow desorption of Pu from colloids could allow Pu sorbed to a colloid to travel much farther than if sorption were an equilibrium process. However, Pu sorption (and particularly desorption) data in the literature are scant and sometimes contradictory. In some cases, Pu desorption is rather fast, with rates dependent on colloid mineralogy.^{3,4,5} Moreover, the effect of sorption and desorption kinetics (as well as other mechanisms) on colloid-facilitated transport at the field scale has not been thoroughly evaluated. This is, in part, due to limitations in colloid transport as well as sorption/desorption models.

In an effort to better understand the dominant mechanisms that control colloid-facilitated Pu transport, we have performed a series of sorption/desorption experiments using mineral colloids and Pu(IV) and Pu(V). We focused on natural colloidal minerals present in water samples collected from both saturated and vadose zone waters at the NTS. These colloid minerals include zeolites, clays, silica, Mn-oxides, Fe-oxides, and calcite. X-ray absorption fine-structure spectroscopy (XAFS) was performed to characterize the speciation of sorbed plutonium. We applied both surface complexation modeling and particle-tracking reactive transport codes to better understand the underlying processes of Pu sorption and desorption and the factors affecting Pu transport at the field scale.

Results

Sorption of Pu(IV) to all mineral colloids examined occurred at a very fast rate (equilibrium reached in ~24 hours). However, the affinity of Pu(IV) for the various minerals varied significantly. At pH 8, sorption to birnessite (Mn-oxide) and goethite (Fe-oxide) was much stronger than to clinoptilolite (a zeolite) and calcite. XANES data showed Pu on the mineral surfaces to be dominated by the Pu(IV) oxidation state. At pH 7-9, aqueous complexation of Pu(IV) with carbonate competes with sorption of Pu(IV) to clinoptilolite resulting in lower sorption (Fig. 1).

Unlike other studies², it appears from our desorption experiments on clinoptilolite that Pu(IV) desorption rates are rather fast. However, the steady state percent that remains sorbed in desorption experiments is significantly higher than in sorption experiments. For example, the free Pu in clinoptilolite desorption experiments between

pH 4-10 ranged from 2 to 8% as opposed to 10 to 30% in sorption experiments. This effect is often observed in sorption/desorption experiments and is described as hysteresis.

While Pu(V) appears to sorb to iron and manganese oxides very quickly, Pu(V) sorption rates are quite slow on aluminosilicates and calcite. Furthermore, XANES data indicate that Pu on all mineral surfaces is dominated by Pu(IV). It appears from our experiments that, in the case of aluminosilicates (and possibly calcite), sorption rates are dependent on Pu(V) disproportionation and reduction in solution and subsequent sorption of Pu(IV). At pH 8, Pu(V) disproportionation and Pu sorption occurred at rates equivalent to a half-life of 0.2 years. For iron and manganese oxides, Pu(V) sorption rates are fast; mineral surfaces appear to sorb Pu(V) directly and promote Pu(V) reduction to Pu(IV).

Discussion

Plutonium redox transformation rates, disproportionation rates, sorption/desorption hysteresis, and other factors may all affect colloid-facilitated Pu transport in the subsurface. Furthermore, the physical aspects of colloid transport (colloid concentration, filtration, stability, etc.) will affect Pu transport. We have applied the mechanistic Pu sorption information in conjunction with colloid filtration to a particle transport code which can account for a number of colloid sorption and filtration mechanisms. A number of simulations were conducted using the particle transport code to interpret field scale implications of laboratory results. Among these was a parametric sensitivity study of transport given a wide combination of forward and reverse sorption rates. This study showed several transport regimes from near-equilibrium to highly kinetic behavior. These simulations provide information regarding the importance of the

various physical and chemical mechanisms on the overall transport of Pu in the subsurface. It appears that observed sorption and desorption rates may be too fast to explain the observed Pu transport at NTS. A particle model that included sorption hysteresis was also tested. Hysteresis effects may better explain the apparent colloid-facilitated Pu transport behavior.

(This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.)

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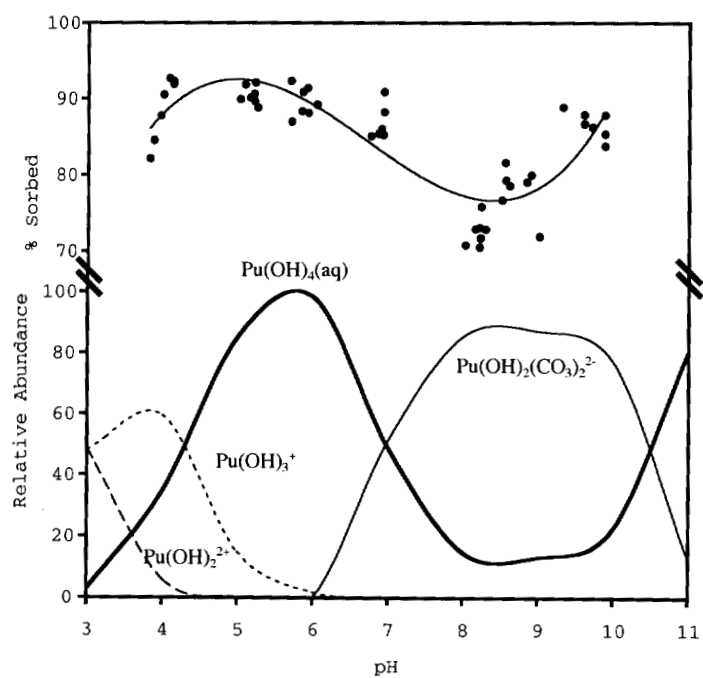


Figure 1. Percent Pu(IV) sorbed and aqueous speciation in clinoptilolite sorption experiments.